ICRN 24

IAPWS Certified Research Need - ICRN

Thermal Conductivity of H_2O at Low Pressures and High Temperatures

The IAPWS Working Group "Thermophysical Properties of Water and Steam" has examined the available experimental and theoretical information for the thermal conductivity of H_2O. The Working Group has concluded that there is a need for:

(a) New experimental measurements for the thermal conductivity of H_2O at low pressures at temperatures up to at least 600 K with an accuracy at the one-percent level

(b) Additional theoretical studies of procedures for calculating the thermal conductivity of H_2O from intermolecular potentials

Although encouraging this work, IAPWS is not able under its statutes to provide financial support. The IAPWS contact can provide any further development information and will liaise between research groups.

Issued by the
International Association for the Properties of Water and Steam

President: **Dr. D.G. Friend**
National Institute of Standards and Technology
325 Broadway
Boulder, CO 80305, USA

Executive Secretary: **Dr. R.B. Dooley**
Structural Integrity Associates, Inc.
Charlotte, NC, USA
Email: bdooley@structint.com

IAPWS Certified Research Need – ICRN

Thermal Conductivity of H_2O at Low Pressures and High Temperatures

The International Association for the Properties of Water and Steam (IAPWS), in collaboration with the International Association for Transport Properties (IATP), has developed new formulations for calculating the transport properties of H_2O. These replace previous formulations based on experimental information available prior to 1980, extending the range of temperatures and densities and making the formulations consistent with the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use [1]. The new correlating equation for the viscosity of H_2O was adopted as the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance [2,3], and that for the thermal conductivity was recently adopted as the IAPWS Formulation 2011 for the Thermal Conductivity of Ordinary Water Substance [4,5].

Meanwhile, Hellmann *et al.* have developed a theoretical procedure for calculating the transport properties from accurate intermolecular potential energies for dilute gases of polyatomic molecules such as CH_4 [6] and H_2O [7]. Specifically, for H_2O they have calculated the shear viscosity, thermal conductivity, self-diffusion, and volume viscosity in the dilute-gas limit at temperatures from 250 K to 2500 K [7] starting from an accurate *ab initio* potential-energy surface for the H_2O pair obtained by Bukowski *et al.* [8].

The theoretical values for the dilute-gas viscosity of H_2O calculated by Hellmann *et al.* [7] are in agreement with the experimental data within their experimental accuracy. They also agree with the new IAPWS formulation for the viscosity of H_2O in the dilute-gas limit within the tolerance of the correlation in the temperature range up to 1173 K covered by the formulation, although the extrapolating behavior of the viscosity to higher temperatures differs somewhat from that obtained by extrapolating the IAPWS formulation beyond its range of validity [3,7].

On the other hand, for the thermal conductivity of H_2O in the dilute-gas limit there are significant discrepancies between the theoretical values and the available experimental data. This is shown in Figure 1, where differences relative to the new IAPWS correlation [4,5] are plotted. At temperatures above approximately 500 K, there is a systematic discrepancy, on the order of 4 %, between the theoretical and most of the experimental values; the IAPWS correlation represents a compromise between the two that attempts to maintain agreement with the experimental data within their expanded uncertainties (which are roughly 3 %).

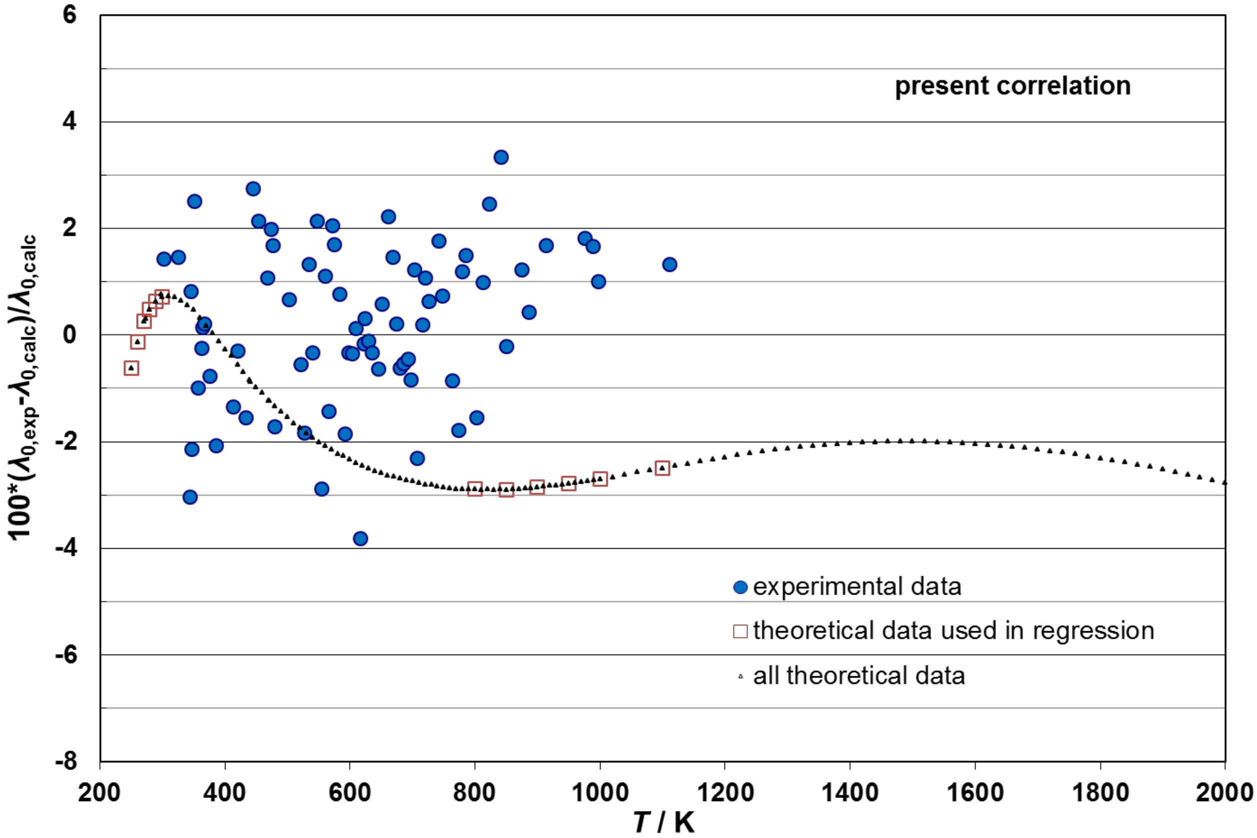

Figure 1. Percent deviation of experimental low-density thermal conductivity data and values calculated from theory [7] from IAPWS formulation for thermal conductivity [4,5]. Figure from Ref. [5]

It is not easy to obtain accurate experimental data for the thermal conductivity in the dilute-gas limit. It is not possible to measure directly the thermal conductivity at zero density. To obtain the thermal conductivity in the dilute-gas limit, one needs to extrapolate from higher pressures or densities. Moreover, some of the experimental data may not be independent from one another [7]. In other cases, one may not have enough information to assess the effect of radiation, temperature jumps, parasitic heat flow, etc. It is therefore in practice not realistic to make an assessment of the accuracies of the published experimental data different from the ones claimed by the investigators. Hence, there is a need for new experimental thermal-conductivity data at high temperatures with an accuracy at the one-percent level. It will not be necessary to measure the thermal conductivity at temperatures all the way up to 1200 K. New experimental data up to at least 600 K could suffice to establish the trend of the temperature dependence of the thermal conductivity at high temperatures.

However, it is not evident *a priori* that the discrepancies at high temperatures must necessarily be attributed to unreliability of the experimental information. An alternative possibility is that the theoretical thermal-conductivity values have a systematic error at the higher temperatures. There seems little reason to doubt the accuracy of the intermolecular potential surface of Bukowski *et* *al.* [8] for H_2O, but it should be remembered that it is a potential for the ground state of the molecule. Deformation of the molecule in higher rotational states at higher temperatures may mean that the rigid-rotor assumption used in the calculations [7] leads to some error. Hence, parallel to an experimental effort, there is also a need for additional theoretical studies to obtain an independent assessment of the actual accuracy with which the thermal conductivity can be calculated from an accurate intermolecular potential energy surface for H_2O in its ground rotational and vibrational state.

Summary of Need

In the case of the thermal conductivity of steam at high temperatures, the available experimental data are in disagreement with the best current theoretical estimates. Improved theoretical work and/or new high-temperature experiments are needed to resolve this discrepancy and reduce the uncertainty in our knowledge of this important property.

References

1. IAPWS, *Revised Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use* (2009), available from http://www.iapws.org.
2. IAPWS, *Release on the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substanc*e (2008), available from http://www.iapws.org.
3. Huber, M.L., Perkins, R.A., Laesecke, A., Friend, D.G., Sengers, J.V., Assael, M.J., Metaxa, I.N., Vogel, E., Mareš, R., and Miyagawa, K., New International Formulation for the Viscosity of H_2O, *J. Phys. Chem. Ref. Data* **38,** 101-125 (2009).
4. IAPWS, *Release on the IAPWS Formulation 2011 for the Thermal Conductivity of Ordinary Water Substanc*e (2011), available from http://www.iapws.org.
5. Huber, M.L., Perkins, R.A., Friend, D.G., Sengers, J.V., Assael, M.J., Metaxa, I.N., Miyagawa, K, Hellmann, R., and Vogel, E., New International Formulation for the Thermal Conductivity of H_2O, *J. Phys. Chem. Ref. Data* **41,** 033102 (2012).
6. Hellmann, R., Bich, E., Vogel, E., Dickinson, A.S., and Vesovic, V., Calculation of the transport and relaxation properties of methane. I. Shear viscosity, viscomagnetic effects, and self-diffusion, *J. Chem. Phys.* **129**, 064302 (2008); *ibid.*, Calculation of the transport and relaxation properties of methane. II. Thermal conductivity, thermomagnetic effects, volume viscosity, and nuclear-spin relaxation, *J. Chem. Phys.* **130**, 124309 (2009).
7. Hellmann, R., Bich, E., Vogel, E., Dickinson, A.S., and Vesovic, V., Calculation of the transport and relaxation properties of dilute water vapor, *J. Chem. Phys.* **131**, 014303 (2009).
8. Bukowski, R., Szalewicz, K., Groenenboom, G.C., and van der Avoird, A., Polarizable interaction potential for water from coupled cluster calculations. II. Applications to dimer spectra, virial coefficients, and simulations of liquid water, *J. Chem. Phys.* **128**, 094314 (2008).

IAPWS Contact:

Dr. Allan H. Harvey
Applied Chemicals and Materials Division
National Institute of Standards and Technology
325 Broadway
Boulder, CO 80305, USA
Tel: +1-303-497-3555
Email: allan.harvey@nist.gov

ICRN Issue Date:	**September 2009**
ICRN Revision Date:	**October 2012**
ICRN Expiration Date:	**September 2015**